

# Density Functional Theory Calculations of Hopping Rates of Surface Diffusion

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Using density-functional theory we compute the energy barriers and attempt frequencies for surface diffusion of Ag on Ag (111) with different lattice constants, and on an Ag adsorbate monolayer on Pt (111). We find that the attempt frequency is of the order of 1 THz for all the systems studied. This is in contrast to the so-called compensation effect, and to recent experimental studies. Our analysis suggests that the applicability of simple (commonly used) scaling laws for the determination of diffusion and growth parameters is often not valid.

68.55.Jk, 68.35.Bs, 68.35.Fx

The determination of the microscopic parameters that govern the evolution and morphology of a growing structure during epitaxy is the focus of a large number of theoretical and experimental studies. However, experimentally deduced values for the diffusion barriers and attempt frequencies often are not measured directly, but result from an analysis of experimental data on the basis of some theoretical model. For example, it is *qualitatively* well established that the density of islands  $N^{\text{is}}$  in growth experiments follows the scaling law<sup>1</sup>

$$N^{\text{is}} = C_0 \left( \frac{D}{F} \right)^{-1/3}. \quad (1)$$

Here  $F$  is the deposition flux,  $D$  is the diffusion constant, and  $C_0$  is a dimensionless quantity that is determined by geometrical factors and parameters that describe the capture efficiency of an island. Recently, Eq. (1) has been applied for a *quantitative* determination of diffusion constants  $D$  for different systems from experimentally measured island densities<sup>2-4</sup>.

Relation (1) is derived under several assumptions, particularly that adatoms are the only species that can diffuse over the surface, i.e., dimers and larger clusters are immobile, and that there is only one mechanism for atomic diffusion, typically assumed to be the hop to a nearest-neighbor lattice site. Then the diffusivity  $D$  is related to the hopping rate of single adatoms by  $D = D_0 \exp(E_d/kT)$ , where  $E_d$  is the energy barrier for surface diffusion and  $D_0 = \Gamma_0 l^2/(2\alpha)$  is the pre-exponential factor. Here  $\Gamma_0$  is called the attempt frequency,  $l$  is the jump length of the diffusing adatom, and  $\alpha$  reflects the dimensionality and symmetry of the motion (for a square lattice  $\alpha = 2$ ). It is commonly assumed that  $\Gamma_0 \sim 10^{12} - 10^{13} \text{ s}^{-1}$ , which is a typical surface phonon frequency. We also note that Eq. (1) is based on the assumption that the so-called critical nucleus is  $i^* = 1$ , which means that dimers and small clusters are stable against break-up. This is the case for typical growth experiments as long as the temperature is low enough or the deposition rate is high enough<sup>5</sup>.

In a recent scanning tunneling microscopy (STM) study Brune *et al.*<sup>4</sup> found that for growth of Ag on a Pt

(111) substrate the size and density of Ag islands changes significantly when one monolayer (ML) of Ag (that grows pseudomorphically on top of the Pt substrate) has been deposited. The density of islands in both cases is different again from the density of Ag islands on top of clean Ag (111). The authors of Ref.<sup>4</sup> analyzed their experimental data with Eq. (1) with the assumption that the mechanism for surface diffusion is hopping of a single adatom to a nearest neighbor site. They obtained the energy barriers and attempt frequencies quoted in Table I, which shows that the attempt frequency found for Ag on 1 ML Ag on Pt(111) is much smaller than that for Ag on Ag (111). A lower attempt frequency for a system with a lower diffusion barrier is not an unexpected result, and is known in the literature as the compensation effect<sup>6</sup>. It can be understood with simple physical arguments that are illustrated in Fig. 1. Consider the solid and the dashed line that are the potential energy curves for a system with a low and with a high barrier. It is evident that the curvature of the potential with the higher barrier is larger at the bottom of the potential well. An atom in a well with a higher curvature vibrates faster, and thus the attempt frequency is larger.

In a molecular dynamics study<sup>7</sup> that employed empirical potentials and the embedded-atom theory it was found that indeed for homoepitaxial diffusion on different metal surfaces there is a systematic compensation effect, i.e., systems that have a larger energy barrier for surface

TABLE I. Results for  $E_d$  and  $\Gamma_0$ . All theoretical values are with  $3N = 15$ , except for Ag on Ag/Pt (111), where  $3N = 27$ . We considered an Ag(111) substrate with tensile (t), compressive (c), and without strain. The substrate Ag(111) (c) was compressed to the lattice constant of Pt.

substrate	experiment <sup>4</sup>		theory (this work)	
	$E_d$ (meV)	$\Gamma_0$ (THz)	$E_d$ (meV)	$\Gamma_0$ (THz)
Ag (111) (t)	–	–	106	0.25
Ag (111)	100	0.2	82	0.82
Ag (111) (c)	–	–	60	1.3
Ag/Pt (111)	60	0.001	60	5.9
Pt (111)	160	10	150	–

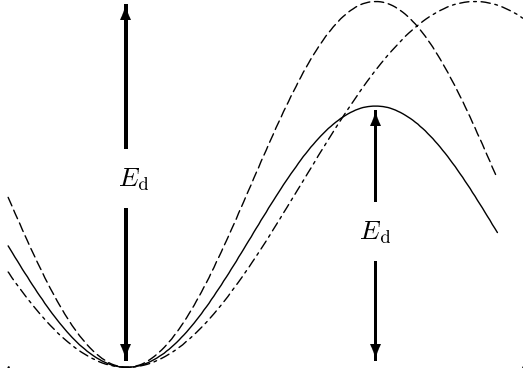


FIG. 1. Schematic illustration of the compensation effect and the anti-compensation effect. When the barrier increases (dashed line compared to solid line), the potential becomes stiffer, and the vibrational frequencies increase. However, when an increase of the barrier is due to an increase in the lattice constant, the curvature of the potential might very well decrease (dashed-dotted line), and as a result the vibrational frequencies decrease. In this simplified picture it is assumed that all the vibrational frequencies at the saddle point increase (decrease) similarly to the ones at the lattice site, and thus all the increases (decreases) of the frequencies in Eq. (1) cancel, except one that corresponds to a vibration in the lattice site.

diffusion have a larger attempt frequency. Values for  $\Gamma_0$  are obtained that vary from  $3 \times 10^{12} \text{ s}^{-1}$  to  $5 \times 10^{13} \text{ s}^{-1}$ , while for the same systems the energy barriers for diffusion increase from 0.05 eV to 0.7 eV. The magnitude of the effect for  $\Gamma_0$  is in the range of typical surface phonon frequencies, and it does not compensate completely (for typical growth temperatures) the increased diffusion barrier. In particular, we note that the attempt frequency is always much larger than the reported value of  $\Gamma_0 = 10^9 \text{ s}^{-1}$  for Ag on 1ML Ag on Pt(111), which is about three *orders of magnitude* smaller than what one would expect. Despite this puzzle, we note that previous theoretical studies seem to suggest that the system 1 ML Ag on Pt (111) behaves rather normal and that, with respect to surface diffusion, it behaves essentially like a laterally compressed Ag (111) substrate<sup>4,8</sup>.

The diffusion constant is determined by the diffusion barrier and pre-exponential factor, but for the latter no *ab initio* calculations have been reported so far. This applies in general, not just to the system of concern in this Letter. In view of the above mentioned puzzle, and similar enigma that seem to exist for other systems, we performed density functional theory calculations of the attempt frequencies for Ag diffusion on Ag (111) with different lattice constants, and on 1 ML adsorbed on Pt (111). We find that in all cases the attempt frequency is of the order of 1 THz, so that claims of a large variation of  $\Gamma_0$  are not supported. We then discuss various mechanisms which become operative in systems with low energy barriers.

TABLE II. The calculated attempt frequency  $\Gamma_0$  for Ag on Ag(111) for different numbers of degree of freedom considered.

$3N$	3	15	99
$\Gamma_0$ (THz)	1.55	0.82	0.71

We employ density-functional theory with the local-density approximation<sup>9</sup>. More details are given in Ref.<sup>8</sup>. Unless noted otherwise, we use a supercell with 4 layers, a  $(2 \times 2)$  surface cell, and the adatom placed on only one side of the slab. Tests have shown that such a cell is large enough<sup>8</sup>.

The energetically most favored adsorption sites are the three-fold coordinated fcc and hcp sites, and an adatom that diffuses from one site to another will pass over the bridge site as the transition state<sup>10</sup>. In principle, the effective diffusion constant on a surface with several adsorption sites within one unit cell needs to be calculated as a combination of the different rates for the motion between the different sites. However, for all the systems studied here the fcc site is always slightly favored over the hcp site (by 5 – 10 meV), but the barrier to hop from an hcp site to an fcc site is almost identical to the one to hop from an fcc site to an hcp site. This provides justification that only the fcc site is considered as the (stable) adsorption site. Transition-state theory (TST) within the harmonic approximation is used, and the attempt frequency is calculated from<sup>11</sup>

$$\Gamma_0 = \frac{\prod_{j=1}^{3N} \nu_j}{\prod_{j=1}^{3N-1} \nu_j^*} \quad (2)$$

The  $\nu_j$  ( $\nu_j^*$ ) are the normal-mode frequencies of the system with the adatom at the fcc site (bridge site), and  $3N$  is the number of degrees of freedom of the system.

We have calculated these normal mode frequencies by first evaluating and then diagonalizing the force-constant matrix. The elements of this matrix are obtained by displacing each individual atom in the cell and calculating the forces that act on all the atoms. An important issue is how large  $3N$  should be for constructing the force-constant matrix. The results obtained for different  $3N$  are summarized in Table II for Ag on Ag (111). If we change  $3N$  from 3 to 15, i.e., take into account the adatom and all atoms in the first layer, the attempt frequency changes from 1.55 THz to 0.82 THz. We also developed a scheme to include a larger number of degrees of freedom, and given in Table II is a value for  $3N = 99$  which corresponds to a  $(4 \times 4)$  surface cell with vibrations of the adatoms and two layers of the substrate. The  $(99 \times 99)$  dynamical matrix was constructed as follows: We use the same force constants as in the  $3N = 15$  situation in the corresponding subspace. For the other force constants we use bulk values (for atoms in the second and deeper layer), and clean-surface values (for farther surface atoms). Tests with a  $(3 \times 3)$  cell revealed that force constants of surface atoms due to the displacement

of atoms that are further away than nearest neighbors are negligible. Similarly, force constants of atoms in the second layer (and below) that result from the displacement of atoms that are further away than its nearest neighbors can be neglected. We estimate that the influence of these negligible force constants on the attempt frequency is less than a factor two, and therefore set them to zero. The attempt frequency for  $3N = 99$  decreases very little compared to the  $3N = 15$  treatment, namely to 0.71 THz, and thus our result obtained when only the adatom is allowed to vibrate is correct within a factor of two.

As argued earlier<sup>4,8</sup>, the main difference between an Ag atom on a clean Ag (111) surface and on 1 ML Ag on Pt (111) is due to strain in the Ag adlayer. We therefore studied the attempt frequencies for Ag on Ag (111) as a function of strain. The results are given in Table I. An increasing lattice constant implies that the diffusion barrier increases<sup>8</sup>, so, according to the compensation effect, the attempt frequency should increase. Surprisingly, the opposite is the case: When the barrier increases from 60 meV to 106 meV, the attempt frequency decreases from 1.3 THz to 0.25 THz. We understand this “wrong trend” as follows: When the diffusion barrier increases because the lattice constant increases, the curvature of the potential decreases, so that the attempt frequency decreases. This anti-compensating effect is sketched schematically in Fig. 1 by the dashed-dotted line.

Our result for Ag on unstrained Ag (111) differs by a factor of  $\sim 4$  from that obtained in the analysis of the experimental data. This difference is partially due to the fact that the analysis of the experimental data ignored that an atom that hops from an fcc site to a neighbor fcc site first visits an hcp site. When the difference in adsorption energies between the fcc and hcp sites is very small, the adatom needs to make (on average) three times as many hopping attempts to get to one of the six adjacent fcc sites than it needs to hop to one of the three adjacent hcp sites. Thus, the attempt frequencies given in Ref. 4, which are also noted in Table I, should be multiplied by a factor of three.

For the diffusion of an Ag adatom on 1 ML Ag adlayer on Pt (111) the experimentally deduced attempt frequency is more than two *orders of magnitude* smaller than that for the Ag (111) surface, but such a reduction is not found in our calculations (compare Table I). When only the adatom and the Ag layer are included we obtain  $\Gamma_0 \simeq 3.8$  THz ( $3N = 15$ ), and upon inclusion of the top Pt layer we obtain  $\Gamma_0 \simeq 5.9$  THz ( $3N = 27$ ). As mentioned earlier, with respect to diffusion energy barriers, the Ag monolayer on Pt (111) behaves very much like a compressed Ag (111) surface. We now find that this also holds for the attempt frequency. The disagreement with the experimentally deduced value, that is three order of magnitude smaller, is significant, and we consider this disagreement a most important result. It demonstrates that the understanding of surface diffusion and growth is far from being complete, although often this is not appreciated. In this regard we note that Eq. (1) is de-

rived under several assumptions, and that often some of them are not met. We will now discuss six different problems which may have troubled the experimental analysis and/or our theoretical results.

*i)* : It is a concern whether the harmonic approximation we used is valid for all the systems under consideration. From the calculation of the forces we find that for the systems studied here the harmonic approximation is indeed a rather good approximation for displacements up to 0.2 Å.

*ii)* : It is known that TST is only working when the following conditions are met: The adatom spends enough time at the adsorption site so that it can equilibrate there. This aspect is connected to the phononic friction, i.e., the strength of the coupling of the adatom vibration to the excitations of the substrate. Additionally, once an atom has crossed the transition site there should be no recrossing before the atom has been equilibrated again. While it is clear that the friction should not be too small or too large, a quantitative criterion when TST is valid is not known<sup>12</sup>. We expect that equilibrium might not be reached when the temperature is too high, but the experiments of Ref.<sup>4</sup> were carried out at temperatures that are smaller than half of the Debye temperature.

*iii)* : Diffusion of small clusters on a metal surface can be significant<sup>14</sup>, but Eq. (1) is only valid when the only mobile species are adatoms. In fact, it has been shown<sup>15</sup> that the scaling exponent in Eq. (1) changes when small clusters are allowed to move and that the island density decreases dramatically<sup>16</sup>. This effect cannot explain the discrepancy we find for the diffusion on Ag/Pt (111): If cluster diffusion were important on Ag/Pt(111) and not (or less) on clean Ag (111), the pre-exponential factor for diffusion on Ag/Pt(111) should be bigger, not smaller, as observed in the experiments. Still, we do not rule out that cluster diffusion plays a role, because it is possible and likely that the diffusivity of cluster diffusion is (very) different to that of single-atom diffusion, and we also note that the exponent in Eq. (1) may change. We are not aware of the direction and size of this effect, but note that cluster diffusion may be particularly important for strained systems and thus Ag diffusion on Ag/Pt(111) is indeed a good candidate.

*iv)* : It has been shown that on metal surfaces the diffusion length may be a multiple of the lateral lattice constant<sup>17,18</sup>. This becomes more relevant when the corrugation of the potential energy surface is less pronounced and the diffusion barrier becomes small<sup>13</sup>, as it is the case for Ag on Ag/Pt(111) and Ag on a compressed Ag (111) substrate. The adatom becomes more delocalized and we speculate that rather than hopping over the surface from one lattice site to an adjacent one, the adatom is “flying” over the surface over several lattice sites. For this process TST is strictly no longer applicable. Moreover, it is conceivable that Eq. (1), particularly its exponent, changes when several diffusion mechanism are operative. We are not aware of the size or direction of such an effect, but under the speculative assumption that the exponent is

reduced by 20%, the discrepancy between the results of Ref.<sup>4</sup> and our calculations could be explained. The analysis of the experimentally measured island density would then yield an activation barrier that it 20% larger, which is supported by experimental<sup>18</sup> and theoretical<sup>19</sup> results for the double-jump of a Pt adatom on Pt(110). This would also explain the good agreement between our calculated and the experimentally deduced diffusion barriers. Additionally, an exponent that it 20% smaller yields an attempt frequency of 1 THz, in agreement with our calculated value.

*v)* : We also note the possibility of diffusion by atomic exchange over long distances. The Ag adlayer is compressed and we speculate that atomic exchange could work such that an atom of the Ag adlayer pops up, becoming an adsorbate atom. Then the vacancy moves towards another adatom (e.g. a long row of Ag adatoms in the Ag adlayer may move). Similar effects have been observed in embedded atom simulations<sup>20</sup>.

*vi)* : Another problem is knowledge of the dimensionless quantity  $C_0$  in eq. (1). An uncertainty in  $C_0$  of one order of magnitude translates into an uncertainty for  $\Gamma_0$  of three orders of magnitude when  $i^* = 1$ . The value of  $C_0$  is essentially determined by the surface geometry and capture efficiency of islands, and with the self consistent approach of Bales and Chrzan<sup>21</sup> one obtains  $C_0 \simeq 0.25$ , which has been used in Ref.<sup>4</sup>. A recent STM study for Pt on Pt(111) used an alternative method to determine  $E_d$  and  $\Gamma_0$ <sup>22</sup>. It is found that  $\Gamma_0 = 5$  THz (an expected result), and from the data in<sup>22</sup> we deduce  $C_0 \simeq 0.28$ . Earlier work<sup>23</sup> suggested that  $C_0$  should be of the order of unity. It is known that often there is *funneling* of adatoms toward step edges. This attraction will become more significant for systems with low diffusion barriers [as it is the case for Ag on 1 ML Ag on Pt (111)], and when surface states are important and affected by adatoms and/or steps.

We conclude that attempt frequencies of single-atom hopping diffusion are indeed of the order of 1 THz and reported deviations from this value, as for example the reduction by three orders of magnitude<sup>4</sup>, are only apparent and actuated by the low energy barrier of diffusion. This implies that adatoms should be described by a more delocalized nuclear wavefunction. Long-range adatom-adatom and atom-step interactions become noticeable, and atomic diffusion proceeds more by “flying” over several lattice constants rather than by hopping to nearest neighbor sites. For strained systems also cluster diffusion may be enhanced. The importance of these effects is difficult to assess by theory, but we trust that more experiments will help to clarify the situation.

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- <sup>1</sup> S. Stoyanov and D. Kachiev, in: Vol. 7 of Current Topics in Material Science, Ed. E. Kaldis (North-Holland, Amsterdam, 1981) ch. 2.
- <sup>2</sup> Y.W. Mo, J. Kleiner, M.B. Webb, and M.G. Lagally, Phys. Rev. Lett. **66**, 1998 (1991).
- <sup>3</sup> J.A. Strosio, D.T. Pierce, and R.A. Dragoset, Phys. Rev. Lett. **70**, 3615 (1993).
- <sup>4</sup> H. Brune, K. Bromann, H. Röder, K. Kern, J. Jacobsen, P. Stoltze, K. Jacobsen, and J. Nørskov, Phys. Rev. B **52**, R14380 (1995).
- <sup>5</sup> C. Ratsch, A. Zangwill, P. Šmilauer, and D.D. Vvedensky, Phys. Rev. Lett. **72**, 3194 (1994).
- <sup>6</sup> W. Meyer and H. Neldel, Z. Tech. Phys. **12**, 588 (1937).
- <sup>7</sup> G. Boisvert, L.J. Lewis, and A. Yelon, Phys. Rev. Lett. **75**, 469 (1995).
- <sup>8</sup> C. Ratsch, A.P. Seitsonen, and M. Scheffler, Phys. Rev. B **55**, 6750 (1997).
- <sup>9</sup> M. Bockstedte, A. Kley, J. Neugebauer, and M. Scheffler, Comput. Phys. Commun. **107**, 187 (1997); <http://www.rz-berlin.mpg.de/th/fhi96md/code.html>.
- <sup>10</sup> Because the bridge site separates an fcc and an hcp adsorption site, the true saddle point is slightly displaced from the bridge site, but we find that in the system studied here this asymmetry is irrelevant.
- <sup>11</sup> G.H. Vinyard, J. Phys. Chem. Solids **3**, 121 (1957).
- <sup>12</sup> As a rule of thumb TST is justified when  $E_d \gg kT$ .
- <sup>13</sup> TST might not be reliable and long jumps become important when the energy of zero-point vibrations is comparable to the energy barrier. For the systems studied here, we estimate this energy to be about 15 meV.
- <sup>14</sup> J.-M. Wen, S.-L. Chang, J.W. Burnett, J.W. Evans, and P.A. Thiel, Phys. Rev. Lett. **73**, 2591 (1994).
- <sup>15</sup> J. Villain, A. Pimpinelli, L. Tang, and D.E. Wolf, J. Phys. I (France) **2**, 2107 (1992).
- <sup>16</sup> L. Kuipers and R.E. Palmer, Phys. Rev. B **53**, R7646 (1996).
- <sup>17</sup> D.C. Senft and G. Ehrlich, Phys. Rev. Lett. **74**, 294 (1995).
- <sup>18</sup> T.R. Linderöth, S. Hørch, E. Lægsgaard, I. Stensgaard, and F. Besenbacher, Phys. Rev. Lett. **78**, 4978 (1997).
- <sup>19</sup> J. Jacobsen, K.W. Jacobsen, and J.P. Sethna, Phys. Rev. Lett. **79**, 2843 (1997).
- <sup>20</sup> N.A. Papanicolaou, (private communication)
- <sup>21</sup> G.S. Bales and D.C. Chrzan, Phys. Rev. B **50**, 6057 (1994).
- <sup>22</sup> M. Bott, M. Hohage, M. Morgenstern, T. Michely, and G. Comsa, Phys. Rev. Lett. **76**, 1304 (1996).
- <sup>23</sup> M.J. Stowell and T.E. Hutchinson, Thin Solid Films **8**, 41 (1971).